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# Non-Aqueous and Crude Oil Foams

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**Résumé — Mousses non aqueuses et mousses pétrolières** — Les mousses produites à partir de systèmes non aqueux sont moins fréquentes que les mousses à base d'eau, mais elles jouent un rôle important dans de nombreuses applications et procédés industriels. La faible tension de surface des liquides à base d'hydrocarbures limite l'adsorption des agents de surface classiques et par conséquent différents composés et méthodes doivent être considérés afin de générer et de stabiliser les mousses à base d'huile. De même, le cassage des mousses non aqueuses indésirables nécessite des considérations spécifiques à ces systèmes. Les mousses de pétrole présentent un intérêt particulier de par leur complexité en raison de la grande variété des composés et des gaz qui peuvent les constituer. Nous présentons dans cet article un aperçu des principaux mécanismes reconnus comme importants pour la stabilité des mousses non aqueuses avec une considération toute particulière pour les mousses de pétrole brut.

**Abstract — Non-Aqueous and Crude Oil Foams** — Foams produced from non-aqueous media are less common than water-based foams but they play an important role in many industries and engineering processes. The low surface tension of hydrocarbon fluids limits the adsorption of common surface activity substances and different compounds and methods must be considered to generate and stabilize oil-based foam. Likewise, the destruction of unwanted non-aqueous based foam requires specific considerations not found with aqueous systems. Of particular interest are petroleum-based foams, which are highly complex due to the wide variety of compounds and gases that can be found. We provide an overview of the major mechanisms known to be important for non-aqueous foam stability with a spotlight on crude-oil foams.

## INTRODUCTION

Foams are an example of two-phase media where gas is dispersed throughout a continuous fluid or solid phase. They are differentiated from simple gas dispersions by their gas-phase volume fraction, which for foam can be conveniently taken as that which exceeds 63 percent for random close-packing of monodisperse hard spheres and 74 percent for ordered close-packing of monodisperse hard spheres. These values are used to characterize the maximum volume fraction of spherical objects and once this is surpassed the dispersed gas bubbles touch and deform, a condition that inevitably provides foam with its unique properties. Furthermore, due to its very high specific surface area foam is not in equilibrium, and its evolution over time is determinant for its use in different applications [1-4].

Both liquid foams as shampoo, dishwashing and shaving foams, and solid as polyurethane or polystyrene foams are found in our everyday activities. Although distinctly different, so-called solid foam is in some respects a subset of liquid foam as before solidification the continuous phase is in a fluid state during foam generation. Thus one finds general concepts relating to foam generation and stability of fluid-based foam pertinent to all types of foam. For example the surface tension will determine the energy required to create a bubble in the media, and the foaming liquid rheology controls the drainage and approach between adjacent bubbles [3, 5, 6]. Beyond these general concepts more specific physical chemical aspects must be addressed to understand individual systems.

By far the most studied and well-understood foaming systems are those based on aqueous-based continuous media [1-3, 7-13]. Generally two types of foam can be identified: short-lived foam whose stability is determined by the drainage rate between adjacent bubbles (*e.g.* champagne foam) and long-lived foam, which relies on energy barriers that prevent bubble coalescence and coarsening (*e.g.* beer foam) [3, 14]. In both systems, the dominant factor is adsorption of surface-active material to the gas-solution interface [15]. During film-drainage between bubbles these surface-active agents modify the no-stress boundary condition at the interface, which dominates the hydrodynamic instability that provokes coalescence of bubbles in pure liquids. In addition, the eventual energy barriers that can prevent coalescence and trap the system in a meta-stable state also arise from material adsorbed to the interface. Indeed the hydrogen bonding responsible for the high surface tension at the water-gas interface makes this interface exceedingly susceptible to adsorption of surface-active components and as such aqueous systems readily produce foam.

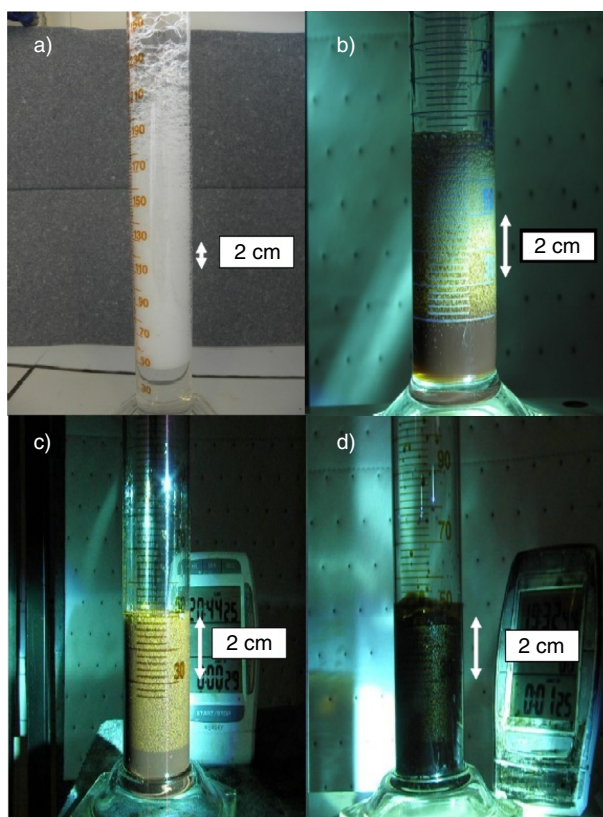


Figure 1

Some different foam systems. a) Aqueous foam made with sodium dodecyl sulfate (concentration of  $8.10^{-3}$  M), b) rapeseed oil foam (doped with a drop of crude oil), c) paraffinic crude oil foam, d) black crude oil foam. Foam a) made with air by simple agitation. Foams b), c) and d) made by depressurisation (5 bar  $\text{CO}_2$ ).

However, other fluids such as hydrocarbons have markedly lower surface tensions and the tendency for adsorption to these interfaces is less, resulting in a much lower foaming propensity (*Fig. 1*).

Non-aqueous hydrocarbon-based liquid foams are not as common as aqueous foams; nonetheless, they play an important role in the cosmetic, petroleum and manufacturing industries. These foams can be used as make-up removers, drilling fluids and solvent-based cleaners. Furthermore, other situations exist where such foams can be detrimental and undesirable, for instance, in crude-oil gas recovery operations or in combustion motors. Thus understanding the unique features of hydrocarbon-based foams can help to improve and promote innovative products and control industrial processes. To this end, in what follows we provide a literature review concerning the generation and stability

of hydrocarbon-based fluid foams with focus on foams related to the petroleum industry.

## 1 MECHANISM FOR STABILIZING NON-AQUEOUS FOAMS

A vast amount of literature focusing on the stabilizing mechanisms in aqueous foams exists [2-4, 9, 11, 12, 16-19] and while the general concepts commonly used to describe aqueous foam and emulsion stability can be useful to understand non-aqueous foams, specific considerations must be taken into account when water is not the continuous media.

The significant difference that sets non-aqueous foaming systems apart is the surface tension at the liquid-gas interface. Typical non-aqueous liquids have a rather low inherent surface tension ( $\sim 15$  to  $30$  mN/m), which is significantly less than that found with water ( $\sim 72$  mN/m). So while in the aqueous foams the added surfactant strongly adsorbs at the interface and significantly reduces surface tension, the rather low level of surface tension of most oils permits little or no adsorption to the surface of hydrocarbon based surfactants. For this reason, Friberg [20] concludes that the surface tension is not a particularly useful analytical tool to help gauge and understand the foaming stability in the case of non-aqueous foams. Furthermore, the importance of electrostatic double-layer repulsion, which can be a dominate stabilizing force in aqueous systems, is insignificant in hydrocarbons due to their low dielectric constants, which limits ion dissociation and prevents significant electrostatic stabilization. Thus it is important to consider just how non-aqueous foam films can be stabilized and what mechanisms resist bubble coalescence.

Although work addressing the stability of non-aqueous foam is limited, three different stabilization sources have been identified: specialty surfactants, multi-phase condensed media, and particle adsorption at the liquid-gas interface. The physical mechanisms attributed in these cases include modification of the surface rheology, steric stabilization and the formation of particulate layers. A summary of the different works performed on non-aqueous foams is given in Table 1.

### 1.1 Specialty Surfactants

Even though the hydrocarbon-gas surface tension is low, certain surface-active molecules can adsorb to this interface and modify its surface rheology. The structure of these compounds is usually complex and many of them have a large molecular weight. The different compounds

that have been identified can be classified in terms of their base molecular structure and include simple hydrocarbons, polydimethylsiloxanes, fluorocarbons, protein-based molecules and asphaltenes:

- hydrocarbon-type surfactants: certain hydrocarbon compounds can act as surfactants at the oil-gas interface [11]. Typically, they are long-chain hydrocarbon molecules with particular functional groups (*e.g.* as acids, alcohol or amine groups). Early work by Sanders [21] reports on the stability of mineral oil and glycol non-aqueous foams stabilized by ethoxylated stearyl alcohol and polyethylene glycol based surfactants. The stability appears to be directly related to the solubility of the surfactant, and highly oil-soluble surfactants do not produce stable foam. This work suggests that the surfactants essentially precipitate at the surface and act as solid stabilizers. Along these lines, Shrestha *et al.* [22-24] have shown that fatty acid esters act as surfactants in different non polar and vegetable oil systems, and that the ester particles can stabilize the foam showing higher stability as their concentration is increased. They note that the particle size plays an important role on the stability – smaller sizes are more effective. To understand the foaming properties of different crude oils, Callaghan *et al.* [25] studied short-chain carboxylic acids. These acids and also phenols with molecular weight  $< 400$  can stabilize so-called evanescent (*e.g.* short-lived) foam, presumably by providing surface tension gradients and/or surface viscosity that alter the non-slip boundary condition during foam-film drainage. Mellema and Benjamins [26] on the other hand have studied the Marangoni effect (*i.e.* flows induced by a surface tension gradient) in sunflower hot oil using phospholipids. They have shown that the stability of oil foams at high temperature is determined by the drainage rate, which is influenced by Bénard-Marangoni convection patterns. They conclude that this effect determines the stability of heated oil foams;
- PolyDiMethylSiloxane (PDMS) based surfactants: the surface activity of PDMS in non-aqueous media can be used to create specialty surfactants to stabilize non-aqueous foam. Combining PDMS with polyols typically does this and these types of surfactants find wide use in polyurethane manufacturing [27]. Low Molecular Weight (MW) PDMS is soluble in many organic solvents and as the MW increases the solubility decreases. The MW range in which the polymer is marginally soluble provides the highest surface activity and can lead to surfactants that stabilize foam. However, while siloxane surfactants can provide moderate foaming, when the MW gets above the marginal solubility limit they can act as foam breakers [11];

TABLE 1  
Summary of works on non-aqueous foams

Authors	Non-aqueous system	Additive	Mechanism of stabilization	References
Sanders	Mineral oil, glycol	Ethoxylated alcohol-PEG surfactant	Precipitation of surfactant (solid stabilizer)	[21]
Friberg and Greene	<i>p</i> -xylene	triethanolammonium	Liquid crystals	[34]
Friberg <i>et al.</i>	Glycerol	Sodium dodecyl sulphate	Liquid crystals	[35]
Shresta <i>et al.</i>	Liquid paraffin, squalane, hexadecane, olive oil	Fatty acid esters	Solid stabilizer lamellar liquid crystal	[22-24, 33]
Mellema and Benjamins	Sunflower oil	Phospholipids	Marangoni effect	[26]
Bergeron <i>et al.</i>	Dodecane	Fluorocarbon surfactants	Gel-like layer at the interface, steric forces	[28]
Binks <i>et al.</i>	26 different oils including non polar and polar oils (pentane, squalane, toluene, ethyleneglycol, formamide, vergetable oils, PDMS, perfluorohexane, etc.)	PTFE and OTFE particles	Stabilization by particles for contact angles between 40 and 90°	[39]
Binks <i>et al.</i>	Lubricating oil	Lubricating additives or particles due to abrasion	Wet transient foams	[40]
Callaghan <i>et al.</i>	Crude oil	Indigenous surfactant	Short-chain carboxylic acids and phenols, dilatational behaviour	[25]
Callaghan and Neustadter				[51]
Adil and Maini	Crude oil	Indigenous surfactant	Asphaltenes	[30]
Zaki <i>et al.</i>	Crude oil and synthetic crude oil	Indigenous surfactants asphaltenes, resins	Viscosity, asphaltene state of aggregation	[29, 62]
Bauget <i>et al.</i>	Synthetic crude oil (toluene)	Asphaltenes, resins	Asphaltenes clusters	[31]

– fluoroalkyl surfactants: due to their fluorocarbon moiety, fluoroalkyl surfactants can reduce the surface tension of liquids to very low values (*e.g.* < 20 mN/m). Prud'homme and Khan [11] has reviewed the effect of fluoroalkyl surfactants on different organic liquids. Using two different types of fluorocarbon surfactants, Bergeron *et al.* [28] studied the stability of dodecane foams in an effort to develop gas-blocking oil foams for Enhanced Oil Recovery (EOR). They found two surfactants that significantly lowered the dodecane-air surface tension and, in one case, stable thin-liquid foam films on the order of 20 nm are formed, while the alternate system produced a gel-like layer at the interface and in the foam film. In both cases, the underlying foam-film stability was attributed to steric forces

arising from overlapping layers of the adsorbed surfactants;

– asphaltenes and resins: asphaltenes and resins that are found in crude oil are composed mainly of polyaromatic carbon ring units with oxygen, nitrogen and sulphur heteroatoms. These compounds are characterized by their solubility in different organic solvents and they are recognized to be responsible for the formation of certain petroleum foams [29]. Adil and Maini [30] suggest that the presence of asphaltenes facilitates the bubble nucleation and protects bubbles from coalescence. Bauget *et al.* [31] have tested toluene solutions with different amounts of asphaltenes and resins to systematically investigate the effect these compounds have on foam lifetime.



In their work, they noticed the existence of a critical concentration of asphaltene (around 10% in toluene) that corresponded to a significant change in the foamability, foam-film lifetime, surface tension and viscoelasticity. These effects were attributed to the formation of asphaltene clusters. They also observed that resins could solubilize asphaltene aggregates, thus by increasing the resins/asphaltene ratio they could decrease the foam lifetime.

## 1.2 Multi-Phase Condensed Media

Friberg [20] has provided a recent review that emphasizes the importance of multi-phase condensed media on non-aqueous foam formation and stability. Sanders [21] who exposed the importance of insoluble surfactant phases and liquid crystals for non-aqueous foam stability discussed this approach earlier. As noted by Friberg [20], the work by Ross and Nishioka [32] involving the foaminess of binary and ternary solutions was instrumental to shedding light on non-aqueous foaming in these situations. In particular, Ross's work demonstrated that in a binary liquid system (diisobutylcarbinol in ethylene glycol), if the lower tension liquid is the minor component in the two-phase combination the system showed foamability. Presumably this is a hydrodynamic phenomenon in which a phase separation at the interface provides viscoelastic forces that stabilize thin-film drainage and allow for transit foam formation. Further developments lead to combining this phenomenon with phase transformation of the minor component at the interface to form liquid crystalline or solid phases that can provide long-term foam stability. More recently, these types of foam have been investigated by Shrestha *et al.* [33]. In their work, liquid crystals are adsorbed onto the surface and change the rheological properties of the lamellar and foam stability increases with the concentration of crystals. Furthermore, Shrestha *et al.* [23, 24] have shown that the stability of non-aqueous foams depends on the surfactant size with smaller sizes producing higher foam stability. Specifically, Friberg and Greene [34] have studied the system triethanolammonium oleate/*p*-xylene showing that if the concentration of *p*-xylene is lower than 3% weight, it behaves as lamellar liquid crystals and if it is higher than 13%, the system is an isotropic liquid. No foam can be achieved in the isotropic liquid but with the crystalline liquid present, the foams obtained have a high stability. In a later work [35], the glycerol/sodium dodecyl sulphate and glycerol/sodium octanoate systems were investigated, showing that the first one creates stable foam, with life times of weeks, stabilized by liquid crystals while the sodium octanoate systems produced unstable foams.

## 1.3 Particle Adsorption

The essentials for understanding foam stabilized by particles were developed long ago during foam flotation operations. Bikerman [36] refers to these as three-phase foams and discusses the importance of the particle wetting properties and size. In such foams, coalescence of the bubbles is prevented or retarded by solid substances partially immersed in the liquid phase. The solid must possess the correct degree of wettability by the liquid phase so that it will remain at the gas-liquid interface rather than being submerged in the bulk liquid. Recent reviews concerning particle stabilized foam and emulsions can be found elsewhere [37, 38]. Binks *et al.* [39] have revisited the effect of using solid particles to stabilize oil foams. They remark that in the case of oil/air interfaces, particles must be partially oleophobic (surfaces coated with fluoro groups can be oleophobic to certain oils) in order to exhibit contact angles between 0° and 180° and stable oil foam forms for contact angles between 40 and 90°. Furthermore, smaller size particles stabilize much more efficiently than larger ones [11]. Stevenson [3] addressed how particles stabilize foam by using maximum capillary pressure arguments to explain the stabilization and observed dependence on particle size. Related to the increased stability by small particles, in the crude oil industry, insoluble nanoaggregates of asphaltene have been found to influence crude-oil foam stability [31].

## 2 NON-AQUEOUS FOAMS: THEIR USES AND INCONVENIENCES

Non-aqueous foams are widely present in industrial processes. The properties of these foams depend on the nature of both bulk phases (continuous and dispersed). One of the most commonly encountered non-aqueous foam occurs in lubricating oil systems [40-42]. The problem in these systems is that air entrained in the oil can subsequently form a foam, causing oxidative and thermal oil degradation, delayed oil supply or even cavitation. The formation of such foams is typically due to additives used in the lubricating oil or particulate matter that develops due to abrasion. The foams formed are usually rather wet (*i.e.* the liquid volume fraction is higher than 20%) and free-flowing. One way to avoid this type of foam calls for using a high solute concentration in the oil phase [40].

Other types of non-aqueous foams are found in the pharmaceutical, personal care and food industry. In these cases, foams have been made using complex multi-component systems (suspensions or emulsions).

In many cases these foams are produced for sensorial aspects and for final product presentation. In the food market, products such as cream desserts are desired for their texture and the effect the presence of gas has on taste and mouth feel. In these cases, proteins and glycosaminoglycans are the most important surfactants.

Another general group of non-aqueous foams are solid foams [3]. These foams are a particular case because the final state of the continuous phase is not liquid. In this group, we can find extruded polymeric foams (*e.g.* extruded polystyrene), metallic foams or ceramic foams. All these foams have an important characteristic in common, before becoming solid foams the continuous phase was initially liquid. The process to convert the non-aqueous foam into a solid varies but usually includes a simple solidification (cooling of the liquid) or a polymeric reaction. For polymeric foams, the continuous phase is a mixture of solvents and reactants that can be triggered based on the chemical system chosen. Once foamed, in some cases a drying step is required to eliminate excess solvent. Direct solvent evaporation without a polymerization step can also be used in some cases. For metallic or ceramic foams, before creating the foam it is necessary to melt the solid phase. After this, gas is introduced through physical or chemical means and the temperature reduced to quench the system and trap the gas before bubble coalescence. By this way, a solid porous structure is obtained.

### 3 PETROLEUM BASED FOAMS AND FOAMY OILS

Petroleum-based foams are one of the most important and abundant types of non-aqueous. Furthermore, the complexity of the continuous phase in these foams is higher than in other non-aqueous foams. This is due to the fact that the composition of crude oil varies greatly depending on the well location and age. Crude oil is a naturally occurring liquid, mineral oil consisting of a variety of organic compounds, mainly saturated and aromatic hydrocarbons, but also more complex compounds such as resins and asphaltenes, which as we have seen previously have amphiphilic properties. The oil industry characterizes the quality of the oil using its API gravity:

$$\text{API gravity } (^{\circ}) = (141.5 / (\text{density at } 60^{\circ}\text{F})) - 131.5$$

A crude with a API gravity less than 10° is denser than water and corresponds to a bitumen, and a crude with a API gravity higher than 31° is a light crude oil. Crude oils with API gravities between 20 and 45° are called

conventional oils and those with API levels lower than 20° are called heavy oils.

Foams can be encountered in any stage of oil recovering and processing and they can be desirable or a nuisance. For example, oil foams can be useful as drilling fluids [43] or gas blocking agents during extraction from porous media [28], but undesirable during gas/oil or oil/water separation and during refining [44-46].

An additional complexity of petroleum foams, apart from oil composition, is that they usually contain water, particles (sand, clay, corrosion products, paraffin crystals, precipitated asphaltenes, etc.) or even additives introduced during the oil extraction phase (surfactants commonly used as bactericides, anti-corrosion, anti-oxidant, emulsion breaker, asphaltene dispersant, anti-scale, etc.). These factors produce petroleum foams that may exhibit several different types of behaviour.

When working with crude-oil foams, it is important to understand certain key definitions:

- “live oil” refers to oil saturated with dissolved gases;
- “dead oil” refers to oil without dissolved gases;
- “foamy oil” is a heavy crude oil that produces stable dispersed bubbles under moderate depressurization and stable foam under severe depressurization.

In fact, in a reservoir, a thermodynamic equilibrium naturally exists between the lightest hydrocarbons (methane, ethane, etc.) dissolved in the oil and the more dense liquid phase. The amount of dissolved gas in the so-called “live oil” is proportional to the temperature and pressure in the system and given by Henry’s law. During live oil extraction, depressurization occurs between the reservoir and the wellhead. The live oil then becomes supersaturated and the system will expel the excess dissolved gas, inducing nucleation and growth of bubbles within the liquid oil phase, modifying its composition as well as its flow properties. In the case of light oils, bubbles coalesce very quickly and a slug flow can appear as large volumes of gas exit the well. However, in the case of heavy oils, bubbles remain dispersed within the oil, leading to a system that resembles “chocolate mousse” and typically referred to as a “foamy oil phenomenon”, even though if a more appropriate term should be “bubbly oil”, as the gas volume fraction is typically found to be between 5 and 40%. This phenomenon appears during higher production rates than expected by reservoir modelling [30, 47-61].

While the foamy-oil flow encountered in many Canadian and Venezuelan heavy-oil reservoirs during production under solution gas drive presents several advantages, both in terms of higher-than-expected well productivity and high primary recovery factor [61], this phenomenon leads to major drawbacks on surface facilities, especially during gas/oil separation.

### 3.1 Factors Contributing to Crude Oil Foam Formation

The amount of foam that a system can create, the stability of the foam and, even, the capacity to create gas/liquid films depend on the characteristics of the gas dissolved. Gases that do not have an affinity for the crude oil tend to form unstable foams. However, if the gas is soluble in the oil, foams can be formed and the extent will depend on the pressure and temperature of the system [18]. The initial Gas to Oil Ratio (GOR) in the crude oil determines the quantity of gas that can be released, which is related to the foam formation. It also bears on foam stability by the number of bubbles and their size distribution [59].

The composition of the crude oil is equally important to the eventual foaming properties. There are several constituents that can promote the formation of foam and/or stabilize it once it is generated. For example, Callaghan *et al.* [25] have found that short-chain carboxylic acids and phenols with a molecular mass lower than 400 are responsible for foam production. Other authors evoke asphaltenes and resins as the primary cause of foam (*Sect. 1.1*). Poindexter *et al.* [62] identified several parameters that are important for controlling the foaming behaviour of crude-oils, which include bulk viscosity and density, oil-gas surface tension, asphaltenes and resins content and their molecular weight.

Viscosity plays an important role in any foam (aqueous or non-aqueous) because it is directly related to the drainage of interstitial fluid in the foam [58-60, 63]. In addition to lowering the drainage rate, high viscosity systems can also lower the rate of gas diffusion between bubbles (Ostwald ripening) and both effects tend to promote foam stability. In fact, Poindexter *et al.* [62] indicate that crude oils with bulk viscosities lower than 150 cP at 37.8°C produce little or no foam. On the other hand, Fraga *et al.* [64] have evaluated high viscosity oils and find that these oils did not generate foams even when they contain high levels of stabilizing species.

As with aqueous foam, the surface properties of liquid-gas interface in crude-oil foam are also important. In particular it has been found that the surface rheological behaviour plays an important role in stabilizing the thin-liquid films in the foam [9, 11, 17, 31, 65].

The presence of other phases apart from oil and gas, such as water or solids, can also influence the foam behaviour and stability. Along these lines Marcano *et al.* [56] have studied the stability of foams formed from Diesel oil and fatty acids surfactants (to simulate Venezuelan crude oils) with dispersed water. They found that it is possible to create stable foam by adding water at concentrations higher than 2%. They suggest that when water is present in the system, the bubbles formed will be

surrounded by water and dispersed in the oil, originating an air/water/oil dispersed system stabilized by the mixture of surfactants, the low molecular weight surfactants being adsorbed at the air/water interface, and the high molecular weight surfactants being adsorbed at the water/oil interface. In their review on foamy oil flow, Sheng *et al.* [66] indicate that the presence of water has no measurable effect on the nucleation of bubbles, hence on bubble frequency but it has an influence on the rheological behaviour of the mixtures. Abivin *et al.* [48] have compared the rheological behaviour of a multi-phase dispersed system, namely gas bubbles and water droplets embedded inside a heavy crude oil, to the one of a system containing only bubbles. They found that the bubbly emulsion is less viscous than the original emulsion. This phenomenon was attributed to the elongation of the gas bubbles, which is facilitated by the high viscosity of the water-in-oil emulsion.

As already mentioned, the presence of solid particles at the interface (sand, aggregates, salts, etc.) can stabilize foam [31, 39, 59]. Furthermore, foam creation and stability can also be enhanced in solid porous media. Sheng *et al.* [59] indicate higher stability foam can be achieved in a porous media than that in a bulk vessel. This effect is a consequence of the wetting behaviour of the media and its subsequent influence on the capillary pressure imposed on the thin foam films.

### 3.2 Tests and Specific Tools for Studying Foaming and Defoaming of Crude Oil

Classical foam tests, such as agitation, Ross-Miles or Bikerman's test [14], have been used in the past to study crude-oil foam. These tests create foams by mechanical agitation or by flowing the gas through the liquid, and were developed for the beer and mineral flotation industry. However, most crude oils are rather viscous and it is hard to adapt these tests to such oils. Moreover the methods do not reproduce the conditions found in the petroleum industry and the type of foam generated is not representative of actual crude-oil foams.

For these reasons, alternative methods have been developed to match field conditions, [59, 64]. Petroleum foam formation during extraction or gas-separation operations is due to rapid depressurisation that causes massive bubble nucleation of dissolved gas, much like that observed when a bottle of champagne is shaken and then abruptly opened. Therefore laboratory foam testing with crude-oil needs to take this key process element into account. As such testing proceeds by first saturating the crude oil under pressure with a desired gas, followed by a procedure to depressurize the system



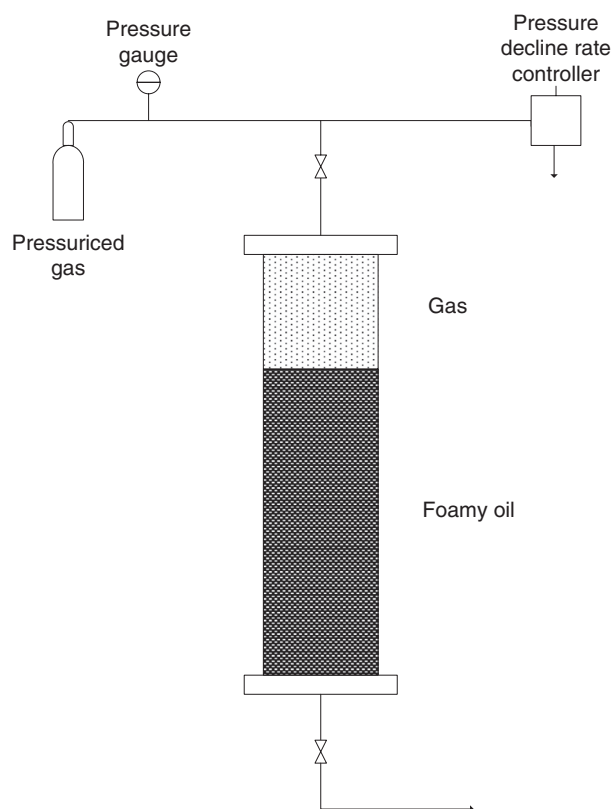


Figure 2

Schema of Sheng's foamy test (from [59]).

under application conditions. As an example, Figure 2 shows a diagram of the experimental apparatus of Sheng *et al.* [59]. In this test, a sample of crude oil ( $20 \text{ cm}^3$ ) is saturated with gas at a high pressure (typically methane at 700 psig) and then transferred to a high pressure cell equipped with a glass window and height graduations. Then the pressure is either reduced suddenly by releasing the gas in the cell, or reduced linearly to a lower pressure by using a pressure decline rate controller. The volume of foamy oil and dispersed gas are estimated by monitoring the crude oil foam height as a function of time. In the test used by Fraga *et al.* [64], gas saturation can be assisted by mechanical agitation and the overall temperature can be controlled to mimic that found in the field. A total of 150 mL of oil is transferred to a compression cell which is sealed and pressurized to the desired pressure. The compression cell is then placed in a roller oven, preheated to the test temperature and then allowed to rotate at 50 rpm for one and two hours. It is then depressurized by opening the outlet valve until 80 mL of foam is sampled in a 100-mL graduated cylinder. The foam height is read as a function of time until total break-up of the foam.

After generating a foam, most experimental methods used to study its evolution are based on an optical measurement of the height of the gas/foam and the foam/oil interfaces. For aqueous and most simple non-aqueous systems, these interfaces are easily discernable (Fig. 1). However, most commercial crude oils are black, and not transparent, which greatly complicates the use of standard optical measurements of the foam levels. For this reason, Pacho and Davies [67] developed sensors using electrical capacitance for detecting and monitoring oil foams. With these sensors they are capable of monitoring the evolution of the foam over time without having to rely on optical tools.

As with aqueous foaming systems, the importance of interfacial rheological properties is well recognized [9, 31, 68]. Surfactant molecules are adsorbed on the liquid-gas interface and decrease their surface tension. The dilatation of these surfaces creates surfactant concentration gradients and hence tension gradients which balance with bulk viscous stress at the surface. This induces an entrainment of the fluid (Marangoni effect) to restore the surfactant concentration equilibrium. For liquid-like interfaces with Newtonian behaviour, the Boussinesq-Scriven law relates stress to the surface rate of deformation *via* the dilatational viscosity and the surface shear viscosity. For elastic interfaces, this relation is described by a general Hooke's law *via* the surface dilatational modulus  $E$  and the surface shear modulus  $G$  [68]. It is also worth noting that the surface mobility/rigidity depends on the surfactant composition. Callaghan *et al.* [65] have used a Langmuir trough and shown that the dilatational surface rheology of the crude oils is an important link to the foam stability. They have also demonstrated that the addition of surfactants (in their work antifoamers) affected the surface rheology of the gas/oil system. Bauget *et al.* [31] have studied the effect that asphaltene and resin concentration has on the properties of toluene mixtures. For concentrations around 10% by weight, they observed a change in the foam properties that correlated with increases in the elastic modulus (determined by the oscillating drop method) and the clustering of asphaltenes. It was postulated that a rigid interface limits bubble rupture leading to more stable foam.

Apart from foam generation and stability, specific efforts have also been carried out to understand crude-oil foam behaviour. For this purpose, rheology is of prime importance to study the flow behaviour of foams [3, 5, 6, 68]. Abivin *et al.* [47] have studied the rheological properties of foamy oil by using a controlled stress rheometer under pressure. Live samples of oil were obtained by recombining a stocked tank oil with methane inside the pressure cell of the rheometer. Rheological measurements

were performed on foamy oil after depressurization. Two different regimes were pointed out: in the first one, under low shear rate, the bubbles remain spherical and induce an increase in the relative foam viscosity; in the second one, under high shear rate, the presence of elongated bubbles leads to a decrease in the apparent viscosity of the material in the flow direction, thus facilitating oil production and transport. The authors suggest that the foamy oil behaves as an anisotropic material, its viscosity being reduced in the flow direction, which facilitates its transport, and increased in the normal direction, which contributes to maintain the bubbles dispersed within the oil. In a later paper [48], the same type of behaviour was evidenced in presence of water droplets.

#### 4 ANTIFOAMING AND DEFOAMING IN THE PETROLEUM INDUSTRY

Dealing with unwanted foams in the oil industry is not simple and a great deal of effort has been carried out to prevent and destroy excessive crude-oil foam. Such foams can reduce oil production capacity, damage equipment, and cause poor oil-gas separation efficiency leading to large overhead losses. Fransen *et al.* [69] expose common foaming problems in the oil industry that include production separators (crude oil), gas sweetening (amine solutions) and gas dehydration (glycol). Issues concerning production separators include [46]:

- foam volume can be larger than liquid volume which requires oversizing of equipment to achieve separation;
- mechanical control of the liquid level is difficult in the presence of foam (any control has to deal with three phases instead of two);
- uncontrolled separators lead to entraining gas in the liquid and/or liquid in the gas outlet.

There are various methods used in foam control, such as breaking the foam by mechanical devices, removing the foamy agents, using process units designed to avoid or to break them, or spreading water over the foam [44, 70]. However, the most common and robust method to control foam is to add antifoaming and defoaming agents [3, 71–76]. For foaming oils, these products are usually silicone oils, particularly PolyDiMethylSiloxane (PDMS) or fluorosilicone products for the most severe cases.

An antifoamer is an additive used to prevent the formation of foam or to reduce the amount of foam that will be created, while a defoamer is an agent added to destroy foams already formed. It is important to note that certain substances can act as a defoamer but not as antifoamer and *vice-versa*. The vast majority of the literature

concerning defoaming and antifoaming substances is focused on the destruction of aqueous foams and as such the development of the mechanisms and criteria for defoaming was done with these systems in mind [77]. One natural question is: can common foam control additives that work for aqueous system also work for crude-oil foams? This can be answered by considering the basic mechanisms and physical chemical criteria that leads to foam destruction. The model used to explain aqueous foam destruction by insoluble oils leads to evaluate three coefficients based on thermodynamic criteria for capillary stability of foam lamellae: the entering coefficient  $E$ , the spreading coefficient  $S$  and the bridging coefficient  $B$  as given by Equations (1) to (3), which are functions of the various surface energies of the system [14, 71]:

$$E_{a/i} = \sigma_{i/g} + \sigma_{i/a} - \sigma_{a/g} \quad (1)$$

$$S_{a/i} = \sigma_{i/g} - \sigma_{i/a} - \sigma_{a/g} \quad (2)$$

$$B_{a/i} = \sigma_{i/g}^2 + \sigma_{i/a}^2 - \sigma_{a/g}^2 \quad (3)$$

where  $\sigma$  is the surface tension and the subscripts  $a$ ,  $g$  and  $i$  refer to the antifoam phase, gas and continuous phase (water or crude oil) respectively.

The primary condition needed to rupture the foam-film is that the antifoaming droplets must enter the gas/liquid interface [71], which is met when the entering coefficient is positive ( $E_{a/i} > 0$ ). Once entry is achieved, two mechanisms can lead to rupture, fluid entrainment and/or pinch-off (Fig. 3):

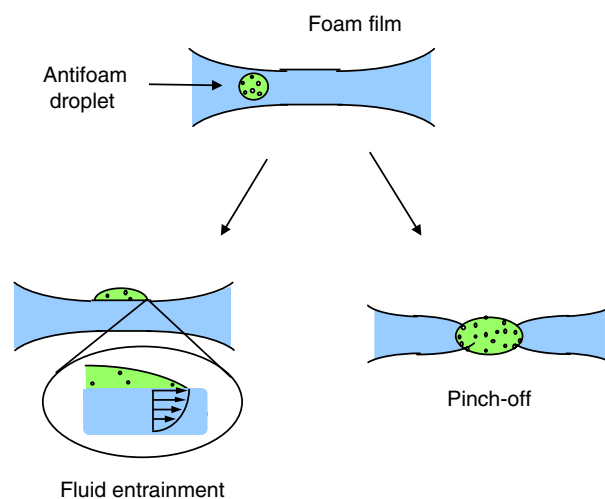


Figure 3

Film-destruction mechanism by PDMS antifoams, from [71].

- fluid entrainment: the antifoam droplet spreads over the gas/liquid interface, ( $S_{a/i} \geq 0$ ), which entrains sub-surface fluid causing local film thinning and rupture;
- pinch-off: after entering, antifoam droplets that form lens can bridge the interface creating a capillary instability that destroys the film by “pinching in off”. This phenomenon was first verified for solid dewetting antifoaming particles. For this to occur in an aqueous system, the contact angle between the gas/antifoam droplet/water ( $\theta_{a/w}^{air}$ ) must be greater than  $90^\circ$ . This contact angle is related to the interfacial tensions, and the condition can be formulated into what is termed by the bridging coefficient ( $B_{a/i} > 0$ ). When this coefficient is positive, the contact angle is greater than  $90^\circ$ .

On the other hand, Denkov [76] differentiates between two types of antifoams: “fast” and “slow”. The main property which differentiates between both types is the barrier to drop entry. The “fast antifoam” is the one whose globules can enter the surfaces and destroy the films in the early stages of film thinning (less than 10 s). The “slow antifoam” is the one which first leaves the foam films and destroys the foam after entering the walls of the Plateau Borders. This entry barrier has been defined as a function of the critical capillary pressure or the disjoining pressure [71, 76, 78–79] where the threshold value of the entry barrier is somewhere between 15 and 20 Pa, which separates the fast antifoam region from the slow one.

Owing to the low surface and interfacial tensions in crude-oil systems it is not obvious that traditional anti-foaming substances based on silicone oils will achieve the criteria needed for the above outlined mechanisms to take place. To evaluate these, typical values of surface tension for water, crude-oil and silicone oil are provided in Table 2, with the associated values of the entering, spreading and bridging coefficients in Table 3.

As can be seen in Table 3, the differences between the various coefficients for aqueous and crude-oil based is pronounced, however the fundamental criteria for film

TABLE 2

Typical values of surface tension, where *g* refers to gas, *o* to crude oil, *s* to silicone and *w* to water

Surface tension	Typical range values (mN/m)
$\sigma_{w/g}$	72 to 30
$\sigma_{w/s}$	4 to 39
$\sigma_{o/g}$	23 to 36
$\sigma_{o/s}$	1.5 to 5
$\sigma_{s/g}$	20

TABLE 3

Values for entering, spreading and bridging coefficients, where *s* refers to silicone, *o* to crude oil and *w* to water

Aqueous system		Oil system	
$E_{s/w}$ (mN/m)	14 to 91	$E_{s/o}$ (mN/m)	4.5 to 21
$S_{s/w}$ (mN/m)	–29 to 48	$S_{s/o}$ (mN/m)	–2 to 14
$B_{s/w}$ ((mN/m) <sup>2</sup> )	516 to 6 350	$B_{s/o}$ ((mN/m) <sup>2</sup> )	131 to 921

rupture can be met in crude-oil systems, indicating that silicone-oil-based antifoams can be effective against crude-oil foam. As with aqueous systems this does not guarantee foam destruction but provides a basis for using these types of antifoams. Other considerations that must also be taken into account when dealing with crude-oil systems are the solubility of the antifoaming agent in the oil, the presence of gels and particles at the gas/liquid interface and effects the additive might have on postprocessing the crude-oil.

Industrial experience confirms that silicone-oil-based systems can be effective at controlling crude-oil foams and they are the most commonly used foam control additives [11, 17]. In certain cases where persistent foam occurs, it is preferable to use fluorinated silicones, which are more efficient due to their high surface activity but which are less affordable. Other molecules that are used include phosphate esters, metallic soaps of fatty acids, sulfonated compounds, amides, polyglycols, glycol ethers and alcohols, either in their pure state or diluted in an adequate solvent [75]. The main advantage is their lower environmental impact because they are more biodegradable than silicones. Furthermore, their impact on refining catalysts is lower because they are less persistent and thermally stable. However, they are generally found much less effective than silicones and are more soluble in oil and therefore are able to interact with the oil and other production chemicals.

It is noteworthy that thus far these additives have been used on a trial-and-error basis without clear guidelines. Optimization and strategies to use these products more effectively will require further detailed systematic studies on the properties of crude-oil-based foams.

## CONCLUSION

Although less common than aqueous-based foam, non-aqueous foam has numerous uses in a broad range of industries. The vast quantity of work on understanding foam has been conducted on aqueous systems and many of the underlying concepts concerning foam generation

and stability can be applied to non-aqueous systems. In both type of systems, high surface viscoelasticity, and barriers that prevent foam-film rupture promote foam stability. However, the low gas/liquid surface tension of non-aqueous systems limits adsorption to their gas/liquid interface and reduces the possibility of generating stable foam films. Certain specialty surfactants have been found to provide stable oil-based foam, and particles having adequate wetting properties can adsorb to the interface and block foam-film rupture. Furthermore, binary liquid systems and multi-phase condensed media have proven to be effective in stabilizing non-aqueous-based foam. Extended these principles to different types of non-aqueous fluids will surely lead to new foaming systems and applications.

Some of the most important and complex non-aqueous foams are found in the petroleum industry. Bituminous, asphaltenic and heavy oils can readily foam upon depressurisation during gas separation processes. These foams can persist for several hours or days delaying the processing of the oil and causing damage to the equipment (corrosion, cavitation, reduction of efficiency, etc.). For this reason it is essential to use additives that prevent the formation of foam (antifoams) or destroy foams already created (defoamers). To date most of the available additives have been optimized for aqueous-based systems and while they can be effective on certain crude-oil foams, particular aspects of the crude oil must be taken into consideration to develop new and more robust foam control formulations.

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